HAL
archives-ouvertes.fr

Smoke toxicity from combustion products based on polymers containing flame retardant additives

Carine Chivas, Jean-Pierre Bertrand, Christian Malvaux, Guy Marlair, Karine Tack

▶ To cite this version:

HAL Id: ineris-00976169
https://hal-ineris.ccsd.cnrs.fr/ineris-00976169

Submitted on 9 Apr 2014

SMOKE TOXICITY FROM COMBUSTION PRODUCTS BASED ON POLYMERS CONTAINING FLAME RETARDANT ADDITIVES

Carine Chivas*, Jean-Pierre Bertrand*, Christian Malvaux*, Guy Marlair** & Karine Tack***
* Accidental Risks Division – Fire department
** Certification Division – Energetic materials
*** Chronic Risks Division – Chemical department
INERIS (Institut National de l'Environnement Industriel et des Risques), France

ABSTRACT

The aim of the study supported by the French Ministry of Ecology and Sustainable Development was to evaluate the technical advantages or drawbacks procured by introducing a flame retardant in a polymer. The incorporation of flame retardants (FRs) presents the advantage of reducing the fire hazard due to flame spread, but might increase the toxicity of fire emissions. In fact, the efficiency of flame retardants is real when the benefits from improvement of the fire resistance properties overbalances the undesired formation of noxious / toxic fumes. The originality of the study is to analyse the presence of toxic fumes as resulting from thermal degradation/combustion reactions of FR polymer systems.

In this paper, we propose to describe preliminary results on the smoke toxicity from binary association of one polymer (polyvinyl chloride) and one typical flame retardant (antimony oxide or aluminum oxide) during combustion. In particular, we report on the interactions between gases (synergistic, additive or antagonist effects), because smoke is confirmed to be the major threat in accidental fires.

The paper is finally a contribution to the analysis of cost/benefit issues of adding FRs in polymer systems considering potential role of related toxic products versus gain in terms of overall fire behaviour.

INTRODUCTION

Polyvinyl chloride (PVC) is an important polymer used in building (pipes, cables, windows...). According to the literature, thermal degradation of PVC begins near 170-200°C. The principal advantage of rigid PVC is the good self resistance to flaming combustion) or the difficulty to burn. However, polymer filled with inorganic additives as antimony oxide (Sb_2O_3) or aluminium trihydroxide (ATH), lead to better properties for technological applications. Moreover, additives in technical PVC products (such as plasticizers, antioxidants dyestuffs...) may in total weight more in mass that the PVC polymer content itself.

Antimony oxide (Sb_2O_3) is widely used as flame retardant additives in combination with halogen compounds. The association of Sb_2O_3 with halogenated systems leads to synergistic effects on flame retardancy. Synergistic effects act principally in gaseous phase, antimony oxide reacts with halogens to give SbX_3 (X : halogen).

Aluminium trihydroxide (ATH or $Al(OH)_3$) is well known to act as a barrier to heat and mass transfer between the polymer and the flame due to formation of a protective ceramic material at the surface layer. The use of flame retardant systems presents the advantage to reduce the fire hazard due to the prorogation, but might increased the toxicity of fire emissions. Therefore, it is necessary to identify the beneficial and adverse true actions of the flame retardant, in terms of, kinetic of inflammation and flame spread on the one hand, and smoke toxicity on the other hand.

REVIEW ON PVC AND FLAME RETARDANTS DEGRADATION STEPS AND SMOKE POLLUTANTS EMITTED DURING COMBUSTION

Thermal degradation of PVC

The combustion reactions of PVC under different fire conditions were studied (among others) by Purser and al. [1]. They showed that the variety of smoke effluents generated during fire depend on the nature of combusting materials and on the burning conditions. This review summarised the main decomposition products from PVC under different fire conditions (Fig. 1.). PVC pyrolyses to form HCl and volatile compounds, which burn and evolve considerable of smoke.
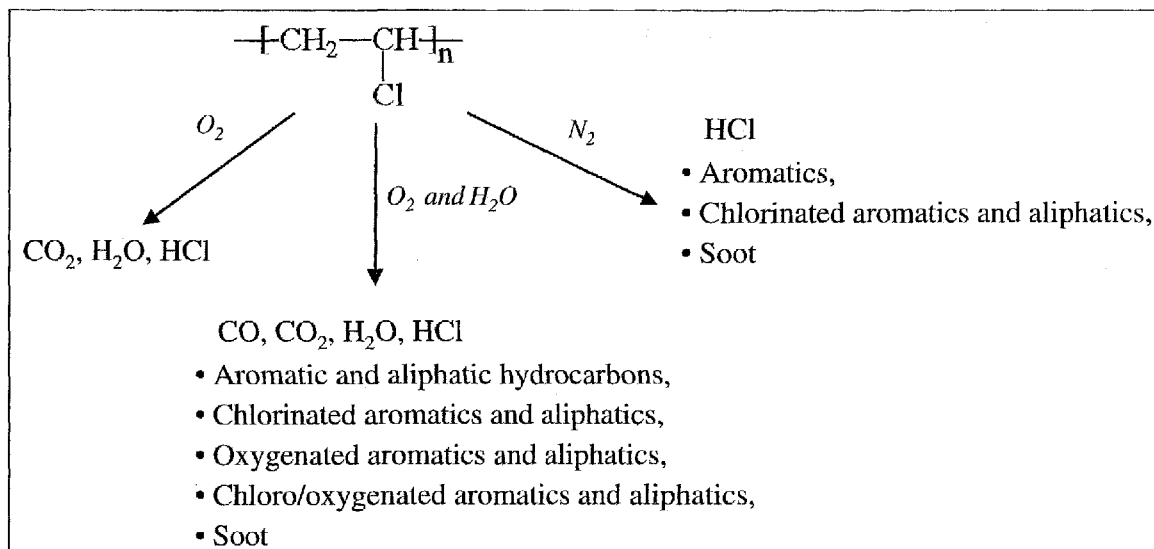
$-[CH_2-CH]_n-$
|
Cl

O_2 → CO_2, H_2O, HCl

O_2 and H_2O →

N_2 → HCl
- Aromatics,
- Chlorinated aromatics and aliphatics,
- Soot

CO, CO_2, H_2O, HCl
- Aromatic and aliphatic hydrocarbons,
- Chlorinated aromatics and aliphatics,
- Oxygenated aromatics and aliphatics,
- Chloro/oxygenated aromatics and aliphatics,
- Soot

Fig. 1 : Combustion products from PVC under different fire conditions [1]

Thermal degradation of flame retardants

For many applications, the use of flame retardant such as antimony oxide or aluminium trioxide are required. According to the literature [2], the antimony trioxide (Sb_2O_3) reacts with HCl emitted from burning PVC to form antimony oxychloride which then decomposes to form antimony trichloride (Fig.2.).

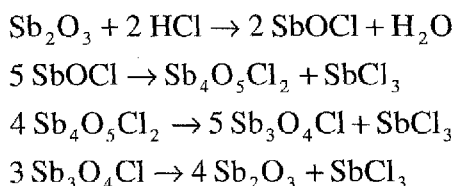$$Sb_2O_3 + 2 HCl \rightarrow 2 SbOCl + H_2O$$

$$5 SbOCl \rightarrow Sb_4O_5Cl_2 + SbCl_3$$

$$4 Sb_4O_5Cl_2 \rightarrow 5 Sb_3O_4Cl + SbCl_3$$

$$3 Sb_3O_4Cl \rightarrow 4 Sb_2O_3 + SbCl_3$$

Fig. 2 : Reactions between antimony trioxide and HCl issue from PVC

The ATH flame retardant mechanism (Fig. 3.) is based on the release of water with cools the flame zone and dilutes active species. Moreover, the formation of Al_2O_3 which contributes to the formation of a ceramic char.
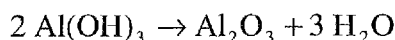
$$2 Al(OH)_3 \rightarrow Al_2O_3 + 3 H_2O$$

Fig. 3 : Thermal decomposition of Aluminium trihydroxide

TEST MATERIALS

The formulations of FR PVCs designated by the letters "A" to "E" in table 1 were supplied by LVM member of Tessenderlo Group. The different test products were manufactured using a blender « Papenmeier » and a hot press moulding (working at 204°C).

Theoretical composition of different formulations according to LVM

Sample (Percentage by weight)	A	B	C	D	E
PVC	86	86.3	84.3	86.3	86.3
CaCO$_3$	11	10.8	10.5	10.8	10.8
OP (One Pack)	3	2.7	2.7	2.7	2.7
Sb$_2$O$_3$	-	0.2	2.5	-	-
Al(OH)$_3$	-	-	-	0.2	2.5

Table 1 : PVC based formulations used as test samples

Elemental composition as analysed by INERIS

| Sample	Mass % of overall sample weight					
	Theoretical elemental composition			As measured from INERIS samples analyses		
	Cl%	Sb%	Al%	Cl%	Sb%	Al%
A	48.81	-	-	45.65 ± 0.17	-	-
B	48.73	0.07	-	44.18 ± 3.10	0.10	-
C	47.58	1.05	-	45.68 ± 0.33	1.80	-
D	48.73	-	0.06	44.70 ± 0.18	-	0.07
E	47.58	-	0.90	44.21 ± 1.21	-	0.80

Table 2 : Theoretical chemical composition of selected formulations

The residual content of aluminium and antimony is null within PVC alone. These results are correlated with the theory. Moreover content of Al and Sb within the other formulations were checked.

EXPERIMENTAL APPARATUS

Tewarson Calorimeter

Experiments were carried out with the Fire Propagation Apparatus implanted at INERIS Fire Laboratory (Fig. 2). The apparatus originally called "50kW lab-scale flammability apparatus" in the USA and Tewarson Apparatus in Europe, is a polyvalent fire calorimeter that was recently described in two standards ASTM E 2058 and NFPA 287 under the final designation Fire Propagation Apparatus (FPA) [3/4].
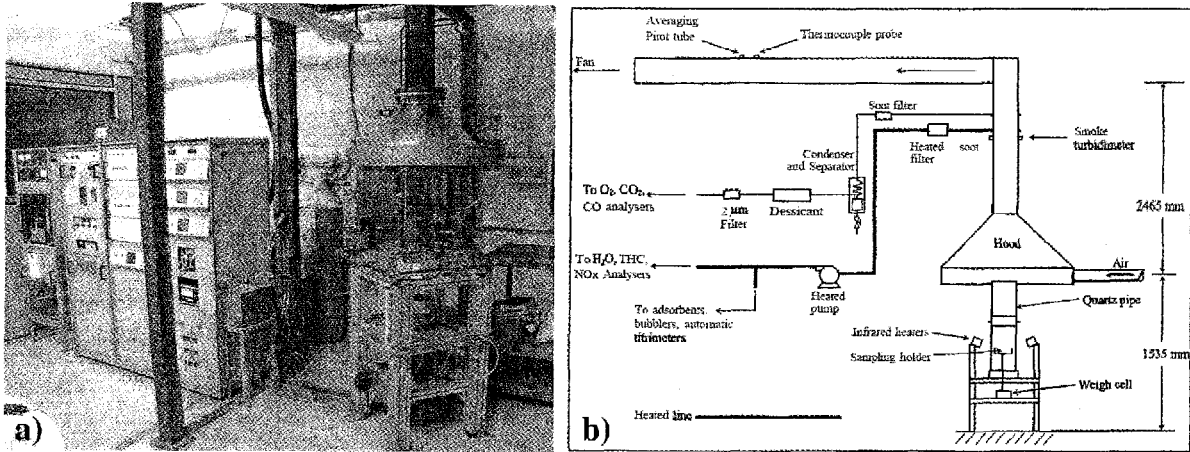
Fig. 2 : Tewarson Calorimeter
a) View of the Tewarson Calorimeter at INERIS, b) Standard characterisation of the composition of fire gases and smoke using the Tewarson Calorimeter

Two mass flow meters allow the operator to set the desired mass flow rate of air of up to 300 Nl.min. Another mass flow meter allow the introduction of CO_2, N_2 or O_2 into the incoming air for non-ambient combustion conditions. The air may be enriched or depleted in oxygen. The composition of oxidising stream is measured by an oxygen analyser, the sample probe is located below the specimen holder in the combustion chamber. The upper part of the calorimeter is the exhaust system with the instrumentation section. Standard characterisation of the composition of fire gases and smoke relies on the routine use of the on-line gas during devices. The heat release rate is measured from both oxygen consumption and carbon dioxide generation calorimetries. The variables measured during a fire test were the mass of the specimen, the concentration of O_2, CO_2, CO, total unburned hydrocarbons (THC), NO, the smoke obstruction at four monochromatic wavelengths, and the temperature.

Recent papers illustrate early experience achieved by INERIS with the described apparatus in collaboration with the Faculté Polytechnique de Mons [5/6]. In collaboration with FM-Global, round robin tests examining the behaviour of non fire retarded plastics, close to pure polymers (including rigid PVC) were also recently presented) [7], as well as contributions to the analysis of the role played by O_2 depletion and air vitiation on global emissions in fires [8].

In the framework of the present study, combustion tests were performed in normal air samples exposed to 50 kW/m^2 to quantify yield of smoke. The sample mass of products submitted to the fire test typically reached some 50 g.

Analytical experiments

Elementary analyses on PVC samples

Total chlorine :

Analyses were performed by volumetric dosage by precipitation (silvermetry) after combustion of the samples in a calorimetric bomb reactor under oxygen atmosphere (P = 30 bars). Reference standard used is ASTM D-808 obs. DIN51577 [9].

Antimony and Aluminium :

Solubilisation of samples were obtained by use of sulfuric acid (H_2SO_4)on hot plates, then in an oven at 550°C. Ashes obtained were dissolved in hot chlorhydric acid.

Analyses were performed by ICP/OES (Inductively Coupled Plasma/Optical Emission Spectrometry). Reference standard used is NF EN ISO 11 885 [10].

Analyses of residues issued from combustion

Total chlorine :

A carbonate fusion pretreatment was necessary to remove organic interferences. After that, analyses were performed by volumetric dosage by precipitation (silvermetry).

Antimony and Aluminium :

Solubilisation of samples were obtained by use of in H_2SO_4 on hot plates, then in an oven at 550°C. Ashes obtained were dissolved in hot chlorhydric acid.

Analyses were performed by ICP/OES (Inductively Coupled Plasma/Optical Emission Spectrometry).

Analyses of Cl, Sb and Al from gaseous emissions during combustion

Cl, Sb or Al containing such emissions were trapped through sampling lines containing suitable solutions in bubblers.

Chlorine :

Analyses were directly performed by volumetric dosage by precipitation (silvermetry).

Antimony and Aluminium :

Analyses were directly performed by ICP/OES (Inductively Coupled Plasma/Optical Emission Spectrometry).

RESULTS AND DISCUSSION

In order to understand the contribution of each component of the FR polymer complex on global smoke toxicity induced by fire a two steps study has been performed. The first part of the study concerns the fire behaviour of polyvinyl chloride alone, the second part deals with the combined components (e.g. polymer matrix + fire retardant) present in the FR plastic.

Results regarding smoke toxicity of several formulations based on PVC are presented in the following sections.

Preliminary observations during combustion tests

First observable phenomenon once external heat at 50 kW/m^2 is applied to PVC samples is surface bubbling due to gas release from the irradiated sample. This gas emission is assumed to be linked with HCl release by chemical bond breakage. After a while, piloted ignition of gases liberated in the course of

the process occurs. Shortly after ignition, abundant black smoke . Char and carbonaceous residues are formed during combustion (Fig. 3).

| PVC |
| PVC + 0.2% Sb_2O_3 |
| PVC + 3% Sb_2O_3 |
| PVC + 0.2% ATH |
| PVC + 3% ATH |
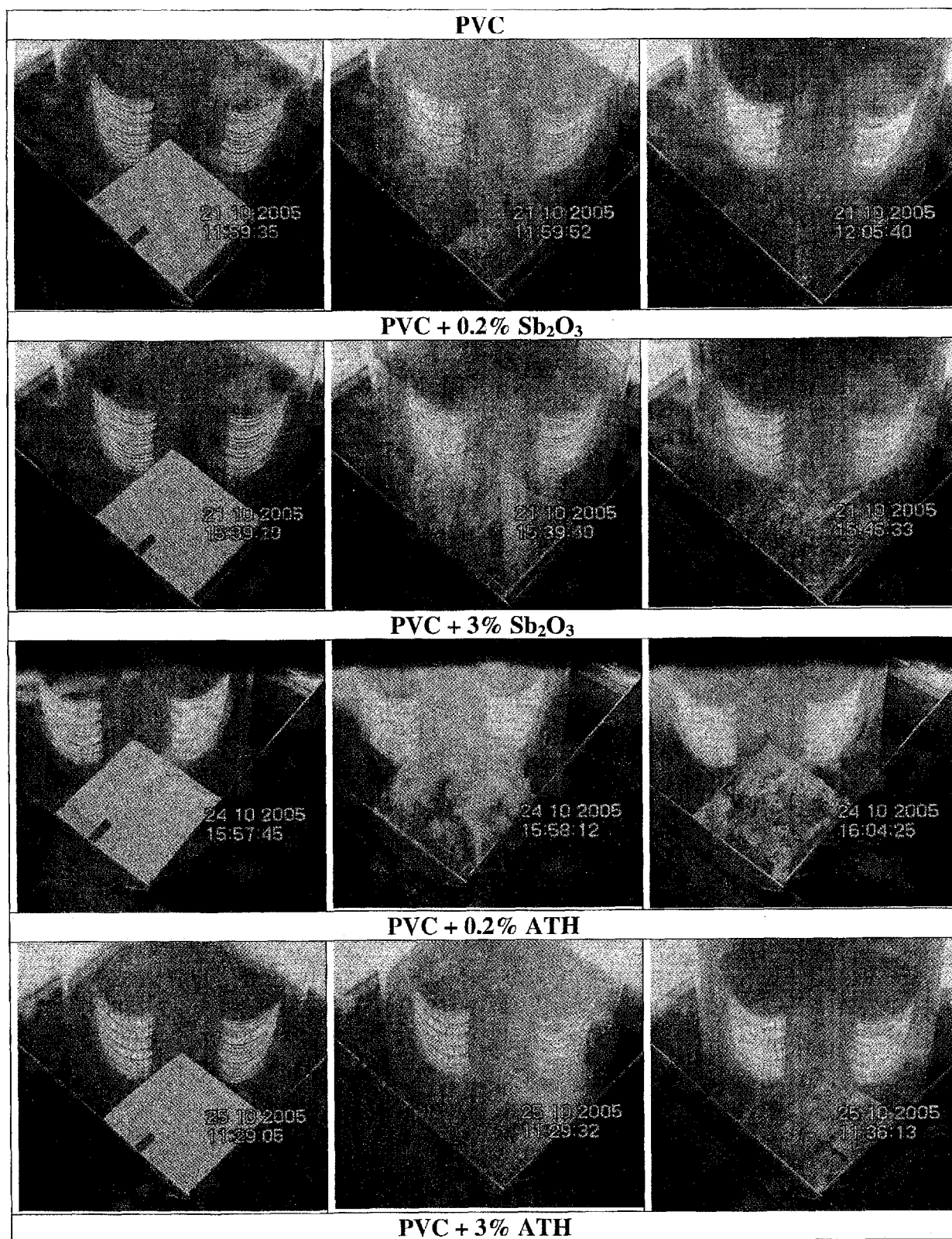
Fig. 3 : Photos collected during Tewarson Calorimeter experiments of PVC, PVC + 0.2% Sb₂O₃, PVC + 3% Sb₂O₃, PVC + 0.2% ATH and PVC + 3% ATH at different phase of combustion

The morphology of the char depends on the additive incorporated in the formulation. In fire conditions, a ceramized char builds on the surface of the formulation containing aluminium trioxide.

Kinetics of combustion and thermal aspects

The Table 3 summarised the main characteristics of combustion : combustion time, burning rate and heat of combustion.

Sample	Combustion time (s)	Average burning rate (g/m²/s)		Effective Heat of combustion * (kJ/kg)	
		$\Delta t_1 = 0$ to 70 s	$\Delta t_2 = 70$ to 350 s	CDG method	OC method
A	500	19.2	6.5	8 380	7 610
B	450	18.6	6.4	7 150	7 180
C	630	15.3	6.9	7 630	7 120
D	510	18.2	6.3	9 620	9 080
E	540	16.1	5.8	8 520	8 600

Table 3 : Kinetics of combustion from PVC formulations

* The effective heat of combustion is measured form both methods, Oxygen Consumption Calorimetry (OC) and Carbon Dioxide Generation Calorimetry (CDG) [11]

The addition of flame retardant (Sb₂O₃ or ATH) in PVC doesn't lead to significant changes in terms of mass loss rate during combustion. The evolution of the burning rate during the combustion is presented on the Fig. 4.This observation is likely to be related to the fact that overall thermal degradation/combustion of the treated FR complex keeps dominated by the role played by HCl liberation in our test conditions. The different formulations presented similar burning rate once steady combustion is achieved. Table 3 gives average burning rates calculated on two different periods of time Δt_1 and Δt_2. Differences are observed mainly at the beginning during preheating/ignition phase. It could be related with the different char structure formed during combustion of the sample. As it is shown on Fig. 3., samples containing ATH lead to a ceramized structure. Moreover, it is well-known that the ATH can decrease the surface temperature and thus delay the pyrolysis of the polymer due to both endothermic decomposition of ATH and heat consumed by water release from the hydroxide.
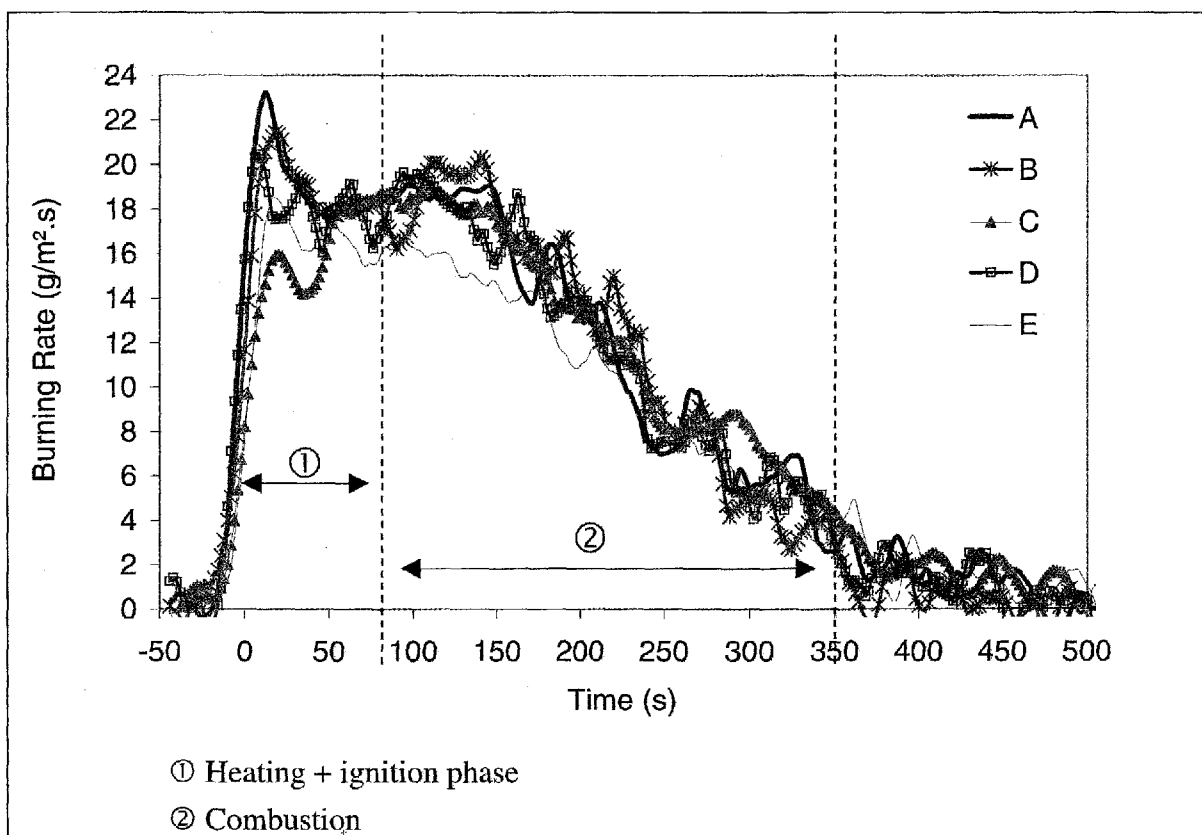
Fig. 4. Burning rate versus time at 50 kW/m² for (A) PVC, (B) PVC + 0.2% Sb₂O₃, (C) PVC + 3% Sb₂O₃, (D) PVC + 0.2% ATH and (E) PVC + 3% ATH

① Heating + ignition phase

② Combustion

Analyses of residues issued from combustion

Sample	Elemental composition of residues		
	Cl%	Sb%	Al%
A	6.30	–	–
B	2.80	0.01	–
C	11.30	0.50	–
D	14.60	–	0.30
E	8.10	–	3.00

Table 4 : Elemental composition of residues issued from combustion of PVC formulations

The influence of the flame retardant additives introduced in the matrix PVC was evaluated by analysis of residues. The analysis of the residues clearly shows, the mechanisms of action of the two FR systems. In addition, the data are consistent with the results obtained concerning the gas pollutants emitted during combustion. Indeed, the recovery of 100% of the initial aluminium from the test sample in the residue allows us to assume that this element doesn't lead to any significant Al-containing gaseous emission in fire conditions. That shows also that the ATH acts in the condensed phase. On the opposite, antimony, acts in the gaseous phase according to reaction mechanisms displayed in figure 2.

Smoke composition : Toxicity of effluents issue from the PVC chloride and flame retardant additive combination during combustion

Table 5 summarises the results from chemical analysis performed by INERIS concerning the emissions of toxic combustion products issue from PVC formulations with and without additives.

Pollutants	Yields of gaseous toxic emission loss (mg/g)				
	A	**B**	**C**	**D**	**E**
CO_2	673	563	581	775	689
CO	62	68	101	68	56
(NO, NO_2)	15	8	10	10	7
methane	3	3	6	2	1
HCt	81	79	151	53	45
HCl	502	504	498	452	499
soot	99	98	77	82	81
Sb [1]	-	0.5	17.6	-	-
$Al(OH)_3$	-	-	-	-	-

[1] counted in Sb_2O_3

Table 5 : Yields of gaseous toxic emission in % by wt. involving from PVC

Pollutants	Theoretical yields of HCl emission (mg/g)				
	A	**B**	**C**	**D**	**E**
HCl (theoretical)	565	550	581	561	576
HCl (experimental)	502	504	498	452	499
Conversion efficiency (%)	89	92	86	81	87

Table 6 : Theoretical yields of HCl emission [12]

This work based on the use of Tewarson calorimeter has aimed to get a first evaluation of main effluents from PVC and PVC containing a flame retardant system (see Table 5).

The objective of this paragraph is to identify the advantages brought by the incorporation of a FR additive (namely Sb_2O_3 or $Al(OH)_3$) in PVC matrix in term of reduction of the " toxicity potential " of the gas effluents emitted in the event of fire.
Given the results obtained so far, the fire retarded effect brought by the additive is not obvious and seems masked by the inherent behavior of the PVC alone which is itself already "fire resistant" due to the presence of the chlorine element.

However, we can notice a plausible benefit effect of ATH in the formulations D and E with a reduction of the total of hydrocarbon (HCt). The use of ATH remaining in condensed phase seems to reduce the yield of HCt emitted wish somewhat contributed to reduce the overall toxic potential of PVC. Naturally, pollution and toxicity issues of PVC, with of without the addition of the studied FRs keep dominated by HCl emissions. It would thus be useful to explore further whether the observation regarding the apparent reduction of HCts is real by performing extra tests with same FRs and other type of technical PVCs and see whether this benefit is extrapolable to other type of polymers. Besides, combining same FRs with other polymer matrices would allow to see if other benefits in terms of reductions of pollutants or toxic yields could be identified.

Table 6 compares measured yields of HCl in our experiments to maximum theoretical yields according to Cl content in PVC test samples. As clearly stated in the literature [12], we found experimental values very close to maximum potential yields.

CONCLUSION AND FURTHER DEVELOPMENT

Tests comparing the overall behaviour of non FR and FR PVC based polymers have been performed making use of the Fire Propagation Apparatus (also called the Tewarson Apparatus). The main goal was to initiate a study aiming at identifying and quantifying the benefit issue of adding FRs in polymers (e.g. gain in terms of fire resistance as compared to potential adverse effect due to potentially increased toxic or pollutant emissions).

At the light of data obtained with binary systems using $Al(OH)_3$ or Sb_2O_3 as the studied flame retardant additive in addition to rigid PVC, preliminary results can be summarized as follows :

- PVC fire retarded or not, are keeps dominated in case of a fire by the mechanism of liberation of HCl due to thermal decomposition.
- In relation with this observation, mass loss rates histories are quite similar whatever are the formulations studied, except during preheating/ignition phase (at list in our experiment).
- In the case of ATH addition, the main apparent benefit lies in some reduction of total hydrocarbons released in the fire gases (to be confirmed with other experiments) ; in addition, the element Al remains 100% in the solid residues.

Tests performed with PVC treated with Sb_2O_3 revealed that part of the Sb is emitted in some form in the fire gases, raising some potential concerns as regard carcinogenic issues.

To go more in depth in the analysis, it is intended to explore the following points :

a) Behaviour of other binary complexes based on PVC (e.g. plasticized PVCs) in addition with the already studied FRs.
b) Influence of the external heat flux applied to discriminate behaviours between FR and non FR PVC based polymers.
c) Benefits of ATH when used as an additive in other polymer matrices (EVA).

This is the workplan we intend to implement in 2006.

REFERENCE LIST

[1] Bernt, A.-S., Keith, P., Purser, D., Combustion atmosphere toxicity of polymeric materials intended for internal cables

[2] Brossas, J., Retardateurs de flammes, Techniques de l'ingénieur AM 3 237 (in French)

[3] ASTM E 2058-00, "Standard Test Method for measurement of Synthetic Polymer Material Flammability Using a Fire Propagation Apparatus (FPA), ASTM, West Conshohocken

[4] NFPA 287, "Standard Test Methods or Measurement of Flammability of Materials in Clean rooms", Using a Fire Propagation Apparatus (FPA), 2000 edition

[5] Brohez, S., Marlair, G., Delvosalle, C., Fire calorimetry relying on the use of the fire propagation apparatus. Part I : early learning from the use in Europe, Fire and Materials. [Accepted 20/04/2005]

[6] Brohez, S., Marlair, G., Delvosalle, C., Fire calorimetry relying on the use of the fire propagation apparatus. Part II : burning characteristics of selected chemical substances under fuel rich conditions, Fire and Materials. [Accepted 20/04/2005]

[7] Marlair, G., Tewarson, A., Effects of the generic nature of polymers on their fire behavior, Fire safety science : proceedings of the 7th International Symposium, 16-21 june 2002, Worcester, USA. International Association for Fire Safety Science, 2003, pp. 629-64

[8] Marlair, G., Bertrand, J-P., Brohez, S., Use of ASTM E 2058 fire propagation apparatus for the evaluation of underventilated fires, Proceedings of the Fire and Materials Conference, 22-23 janvier 2001, San Francisco, Etats-Unis, pp. 301-313

[9] ASTM D-808 obs. DIN51577 : sulfur and halogens/chlorine in petroleum products (bomb method)

[10] NF EN ISO 11885 (1998), Qualité de l'eau - Qualité de l'eau - Dosage de 33 éléments par spectroscopie d'émission atomique avec plasma couplé par induction (ISO 11885:1996), p.18

[11] Brohez, S., Marlair, G., Delvosalle, C., Tewarson, A., The measurement of heat release from oxygen consumption in sooty fires, Journal of Fire Sciences, 2000, vol. 18, pp. 327-353

[12] Terrill, J.B., Montgomery, R.R., Reinhardt, C.F., Toxic gases from fires, Science, Vol. 200, N°4348 (1978)